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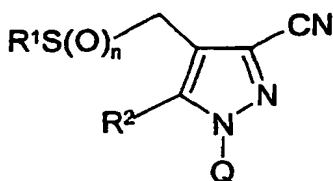
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(54) Title: **3-THIOMETHYLPYRAZOLES AS PESTICIDES**



(I)

(57) Abstract: The invention relates to 4-thiomethylpyrazole compounds of formula (I): wherein R¹, R², Q and n are as defined in the description, and to their use as pesticides.

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Description

3-THIOMETHYLPYRAZOLES AS PESTICIDES

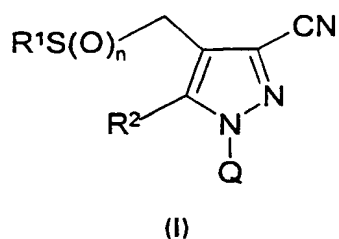
The invention relates to 4-thiomethylpyrazole compounds, compositions containing them, processes for their preparation, and their use for the control of arthropod pests (especially insects) and nematodes.

Insecticidal pyrazole compounds with a thioamide substituent in the 3 position of the pyrazole ring are disclosed in WO-A 99/62886.

However, since modern insecticides must meet a wide range of demands, for example regarding level, duration and spectrum of action, use spectrum, toxicity, combination with other active substances, combination with formulation auxiliaries or synthesis, and since the occurrence of resistances is possible, the development of such substances can never be regarded as concluded, and there is constantly a high demand for novel insecticides which are advantageous over the known ones, at least as far as some aspects are concerned.

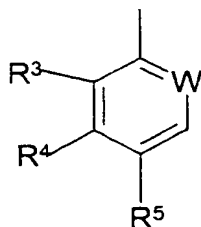
It was an object of the present invention to provide compounds which widen the spectrum of existing pesticides in various aspects.

The present invention provides a compound of formula (I):

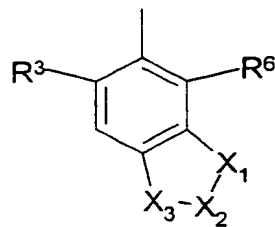


wherein:

Q is a group (A1) or (A2):



(A1)



(A2)

W is N or CR⁶;

-X₁-X₂-X₃- is -CF₂CF₂O-, -CF₂OCF₂- or -OCF₂O-;

R¹ is alkyl, haloalkyl, alkenyl, haloalkenyl, alkynyl, haloalkynyl, cycloalkyl, cycloalkylalkyl or -(CH₂)_mR⁷; or is naphthyl optionally substituted by alkyl, haloalkyl, halogen, NO₂, alkoxy, haloalkoxy or R⁸S(O)_p;

R² is hydrogen, halogen or optionally substituted amino;

R³ and R⁶ are each independently hydrogen or halogen;

R⁴ is hydrogen or haloalkyl;

R⁵ is hydrogen, halogen, haloalkyl, haloalkoxy, -S(O)_pCF₃ or SF₅;

R⁷ is phenyl or a five to seven membered heteroaromatic ring containing from one to four heteroatoms which may be the same or different selected from nitrogen, oxygen and sulphur, which ring is optionally substituted by R⁹;

R⁸ is alkyl or haloalkyl;

R⁹ is alkyl, haloalkyl, halogen, CN, NO₂, R¹⁰O, R⁸S(O)_p, C(O)R⁸, C(O)OR¹⁰ or

NR¹⁰R¹¹; or when R⁷ is phenyl two adjacent R⁹ groups together form a -CF₂OCF₂- or -OCF₂O- group;

R¹⁰ and R¹¹ are each independently hydrogen, alkyl or haloalkyl; and

m, n and p each independently have the values zero, one or two; or an agriculturally acceptable salt thereof.

The 4-thiomethylpyrazoles and the agriculturally acceptable salts thereof as defined above, possess valuable pesticidal properties. The compounds of the invention show improved pesticidal activity in comparison with known compounds.

The invention also encompasses any stereoisomer, enantiomer or geometric isomer, and mixtures thereof.

By the term "agriculturally acceptable salts" is meant salts the cations or anions of which are known and accepted in the art for the formation of salts for agricultural or horticultural use. Suitable salts with bases include alkali metal (e.g. sodium and potassium), alkaline earth metals (e.g. calcium and magnesium), ammonium and amine (e.g. diethanolamine, triethanolamine, octylamine, morpholine and dioctylmethylamine) salts. Suitable acid addition salts, e.g. formed by compounds of formula (I) containing an amino group, include salts with inorganic acids, for example hydrochlorides, sulphates, phosphates and nitrates and salts with organic acids for example acetic acid.

Unless otherwise specified alkyl, acyl and alkoxy groups (or portions thereof) may be straight- or branched- chain and have from one to ten (preferably one to six) carbon atoms.

Cycloalkyl groups have from three to six carbon atoms in the ring and may be substituted by alkyl or halogen.

Alkenyl and alkynyl groups or portions thereof may be straight- or branched- chain and have from two to eight (preferably two to four) carbon atoms.

The term "halo" before the name of a radical means that this radical is partially or completely halogenated, that is to say, substituted by F, Cl, Br, or I, in any combination, preferably by F or Cl. The term "halogen" means F, Cl, Br or I.

A preferred embodiment of the invention comprises a compound of formula (I) wherein Q, R¹ and n are as defined above and R² is -NR¹²R¹³ or -N=C(R¹⁰)(R¹⁴), wherein: R¹² and R¹³ are independently selected from hydrogen, alkyl, haloalkyl, alkenyl, haloalkenyl, alkynyl, haloalkynyl, -C(O)R¹⁵ and C(O)OR¹⁵; or R¹² and R¹³ are joined together forming a divalent radical having 4 to 6 atoms in the chain, this divalent radical being alkylene, alkyleneoxyalkylene or alkyleneaminoalkylene (preferably to form a morpholine, pyrrolidine, piperidine or piperazine ring);

R¹⁴ is alkoxy or haloalkoxy; or is phenyl optionally substituted by alkyl, haloalkyl, hydroxy, halogen, alkoxy, -S(O)_pR⁸ or CN;

R¹⁵ is alkenyl, haloalkenyl, alkynyl or haloalkynyl; or is alkyl optionally substituted by halogen, alkoxy, C(O)R⁸, C(O)OR¹⁰, CN, -S(O)_pR⁸, or CONR¹⁰R¹¹.

Preferred compounds of formula (I) are those in which R¹ is alkyl, haloalkyl, cycloalkyl or naphthyl; or phenyl optionally substituted by halogen, alkyl, haloalkyl, alkoxy,

haloalkoxy or NO_2 ; or pyridyl optionally substituted by halogen or haloalkyl; or $-\text{CH}_2\text{R}^7$ where R^7 is phenyl optionally substituted by halogen, alkyl or alkoxy; or $-\text{CH}_2\text{CH}_2\text{R}^7$ where R^7 is phenyl.

Preferred compounds of formula (I) are those in which Q is a group (A1) wherein:

W is N or CR^6 ; R^3 and R^6 are each independently hydrogen or halogen; R^4 is hydrogen; and R^5 is halogen, CF_3 , OCF_3 or SF_5 ; or wherein:

W is N or CR^6 ; R^3 and R^6 are each independently hydrogen or halogen; R^4 is CF_3 ; and R^5 is hydrogen.

More preferred compounds of formula (I) are those in which Q is a group (A1) wherein:

W is CR^6 ; R^3 is hydrogen or halogen; R^6 is halogen; R^4 is hydrogen; and R^5 is halogen, CF_3 or OCF_3 ; or wherein:

W is CR^6 ; R^3 is hydrogen; R^6 is halogen; R^4 is CF_3 ; and R^5 is hydrogen.

Preferred compounds of formula (I) are those in which R^2 is $-\text{NR}^{12}\text{R}^{13}$ or $-\text{N}=\text{C}(\text{R}^{10})(\text{R}^{14})$.

More preferred compounds are those in which R^2 is $-\text{NR}^{12}\text{R}^{13}$ or $-\text{N}=\text{C}(\text{R}^{10})(\text{R}^{14})$, wherein R^{12} is hydrogen, alkyl or $-\text{C}(\text{O})\text{R}^{15}$; R^{13} is hydrogen or alkyl; R^{10} is hydrogen; R^{14} is alkoxy; and R^{15} is alkyl.

Yet more preferred compounds are those in which R^2 is $-\text{NHR}^{13}$ or $-\text{N}=\text{CH}(\text{R}^{14})$; wherein R^{13} is hydrogen or alkyl; and R^{14} is alkoxy.

Compounds in which R^2 is amino are most preferred.

Compounds in which n is 1 or 2 are also preferred.

A preferred class of compounds of formula (I) are those in which:

R^1 is alkyl, haloalkyl, cycloalkyl or naphthyl; or phenyl optionally substituted by halogen, alkyl, haloalkyl, alkoxy, haloalkoxy or NO_2 ; or pyridyl optionally substituted by halogen or haloalkyl; or $-\text{CH}_2\text{R}^7$ where R^7 is phenyl optionally substituted by halogen, alkyl or alkoxy; or $-\text{CH}_2\text{CH}_2\text{R}^7$ where R^7 is phenyl;

Q is a group (A1) wherein:

W is N or CR⁶; R³ and R⁶ are each independently hydrogen or halogen; R⁴ is hydrogen; and R⁵ is halogen, CF₃, OCF₃ or SF₅; or wherein:

W is N or CR⁶; R³ and R⁶ are each independently hydrogen or halogen; R⁴ is CF₃; and R⁵ is hydrogen; and

R² is -NR¹²R¹³ or -N=C(R¹⁰)(R¹⁴); wherein R¹² is hydrogen, alkyl or -C(O)R¹⁵; R¹³ is hydrogen or alkyl; R¹⁰ is hydrogen; R¹⁴ is alkoxy; and R¹⁵ is alkyl.

A further preferred class of compounds of formula (I) are those in which:

R¹ is alkyl, haloalkyl, cycloalkyl or naphthyl; or phenyl optionally substituted by halogen, alkyl, haloalkyl, alkoxy, haloalkoxy or NO₂; or pyridyl optionally substituted by halogen or haloalkyl; or -CH₂R⁷ where R⁷ is phenyl optionally substituted by halogen, alkyl or alkoxy; or -CH₂CH₂R⁷ where R⁷ is phenyl;

Q is a group (A1) wherein:

W is N or CR⁶; R³ and R⁶ are each independently hydrogen or halogen; R⁴ is hydrogen; and R⁵ is halogen, CF₃, OCF₃ or SF₅; or wherein:

W is N or CR⁶; R³ and R⁶ are each independently hydrogen or halogen; R⁴ is CF₃; and R⁵ is hydrogen;

R² is -NR¹²R¹³ or -N=C(R¹⁰)(R¹⁴); wherein R¹² is hydrogen, alkyl or -C(O)R¹⁵; R¹³ is hydrogen or alkyl; R¹⁰ is hydrogen; R¹⁴ is alkoxy; and R¹⁵ is alkyl; and n is 1 or 2.

A further preferred class of compounds of formula (I) are those in which:

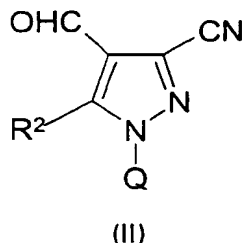
R¹ is alkyl, haloalkyl, cycloalkyl or naphthyl; or phenyl optionally substituted by halogen, alkyl, haloalkyl, alkoxy, haloalkoxy or NO₂; or pyridyl optionally substituted by halogen or haloalkyl; or -CH₂R⁷ where R⁷ is phenyl optionally substituted by halogen, alkyl or alkoxy; or -CH₂CH₂R⁷ where R⁷ is phenyl;

Q is a group (A1) wherein:

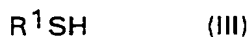
W is CR⁶; R³ is hydrogen or halogen; R⁶ is halogen; R⁴ is hydrogen; and R⁵ is halogen, CF₃ or OCF₃; or wherein:

W is CR⁶; R³ is hydrogen; R⁶ is halogen; R⁴ is CF₃; and R⁵ is hydrogen; and R² is -NHR¹³ or -N=CH(R¹⁴); wherein R¹³ is hydrogen or alkyl; and R¹⁴ is alkoxy.

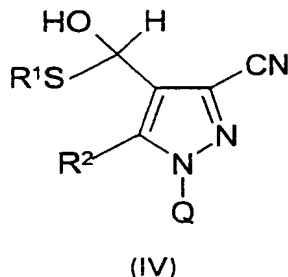
The compounds of general formula (I) can be prepared by the application or adaptation of known methods (i.e. methods heretofore used or described in the chemical literature. Compounds of general formula (I) wherein R^1 , R^2 and Q are defined above and n is zero may be prepared by the reaction of a compound of formula (II):



wherein R^2 and Q are defined above, with a thiol of formula (III):



wherein R^1 is as defined above, in the presence of a Lewis acid, preferably boron trifluoride etherate, to give a hemithioacetal intermediate of formula (IV):



which is not generally isolated, and is treated in situ with a reducing agent generally a hydrosilane derivative (i.e. a silane which contains one or more hydrogen atoms), preferably a trialkylsilane such as triethylsilane. The reaction is generally performed in a chlorinated solvent such as 1,2-dichloroethane, at a temperature of from 0° to 60°C. Compounds of general formula (I) wherein R^1 , R^2 and Q are defined above, and n is 1 or 2 may be prepared by oxidising a corresponding compound in which n is 0 or 1. The oxidation is generally performed using a peracid such as 3-chloroperbenzoic acid in a solvent such as dichloromethane, or with hydrogen peroxide generally in the presence of trifluoroacetic acid, at a temperature of from 0°C to the reflux temperature of the solvent.

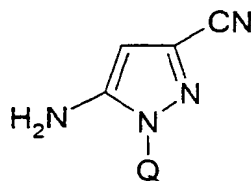
These processes are also an object of the invention.

Compounds of general formula (I) wherein R^1 , Q and n are as defined above, and R^2 is as defined above with the exclusion of amino, may be prepared from the corresponding

compounds in which R² is amino by the application of known methods for example as described in European Patent Publication Numbers 0234119, 511845, 352944 and 295117.

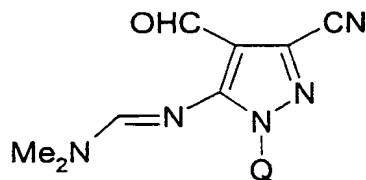
If desired, a 4-thiomethylpyrazole of formula produced by any of the above process embodiments may be converted into an agriculturally acceptable salt thereof.

Intermediates of formula (II) wherein R² is amino are known or may be prepared by known methods, for example by the Vilsmeier formylation of compounds of formula (V):



(V)

using phosphoryl chloride and N,N-dimethylformamide at a temperature of from 0° to 50°C to give a compound of formula (VI):



(VI)

which is hydrolysed, generally under acidic conditions, for example using hydrochloric acid, in a solvent such as tetrahydrofuran at a temperature of from 0° to 100°C.

Intermediates of formula (III) and (V) are known or may be prepared by known methods.

The invention is illustrated by the following non-limiting examples, and in the tables it will be understood that 'Me' means methyl, 'Et' means ethyl, 'i-Pr' means isopropyl 't-Bu' means tert butyl, and 'Ph' means phenyl.

Example 1

2-Methylbutanethiol (0.327mmol) was added to a solution of 1-(2,6-dichloro-4-trifluoromethylphenyl)-3-cyano-4-formylpyrazole (0.297mmol) in 1,2-dichloroethane. A solution of boron trifluoride etherate (2.0 ml of a 3.75% (v/v) solution in 1,2-dichloroethane), then triethylsilane (1.0 ml of a 7.08% (v/v) solution in 1,2-dichloroethane) was added and the mixture stirred at 20°C overnight. The mixture was evaporated, redissolved in N,N-dimethylformamide and purified by LC/MS using a

methanol/water gradient to give 5-amino-1-(2,6-dichloro-4-trifluoromethylphenyl)-3-cyano-4-(2-methylbutylthiomethyl)pyrazole (Compound 1, 0.15 mmol), MS 437.

By proceeding in a similar manner the following compounds of formula (I), shown in Table 1 in which R² is amino and n is zero were also prepared.

Table 1

Cpd No.	R1	Q	MS
2	methyl	2,6-Cl ₂ -4-CF ₃ Ph	381
3	cyclopentyl	2,6-Cl ₂ -4-CF ₃ Ph	435
4	cyclohexyl	2,6-Cl ₂ -4-CF ₃ Ph	449
5	1,1-Me ₂ -propyl	2,6-Cl ₂ -4-CF ₃ Ph	437
6	isopropyl	2,6-Cl ₂ -4-CF ₃ Ph	409
7	1-Me-propyl	2,6-Cl ₂ -4-CF ₃ Ph	423
8	benzyl	2,6-Cl ₂ -4-CF ₃ Ph	457
9	3-Me-butyl	2,6-Cl ₂ -4-CF ₃ Ph	437
10	4-Cl benzyl	2,6-Cl ₂ -4-CF ₃ Ph	491
11	4-OMe benzyl	2,6-Cl ₂ -4-CF ₃ Ph	487
12	2-Me-propyl	2,6-Cl ₂ -4-CF ₃ Ph	423
13	ethyl	2,6-Cl ₂ -4-CF ₃ Ph	395
14	propyl	2,6-Cl ₂ -4-CF ₃ Ph	409
15	3-Cl-propyl	2,6-Cl ₂ -4-CF ₃ Ph	443
16	butyl	2,6-Cl ₂ -4-CF ₃ Ph	423
17	pentyl	2,6-Cl ₂ -4-CF ₃ Ph	437
18	4-Me benzyl	2,6-Cl ₂ -4-CF ₃ Ph	471
19	4-t-butyl benzyl	2,6-Cl ₂ -4-CF ₃ Ph	513
20	CH ₂ CF ₃	2,6-Cl ₂ -4-CF ₃ Ph	449
21	CH ₂ CHCl ₂	2,6-Cl ₂ -4-CF ₃ Ph	464
22	2-naphthyl	2,6-Cl ₂ -4-CF ₃ Ph	493
23	Ph	2,6-Cl ₂ -4-CF ₃ Ph	443

Cpd No.	R1	Q	MS
24	2,5-Cl ₂ Ph	2,6-Cl ₂ -4-CF ₃ Ph	512
25	2-OMe Ph	2,6-Cl ₂ -4-CF ₃ Ph	473
26	2-i-Pr Ph	2,6-Cl ₂ -4-CF ₃ Ph	485
27	2-Me Ph	2,6-Cl ₂ -4-CF ₃ Ph	457
28	3,4-Cl ₂ Ph	2,6-Cl ₂ -4-CF ₃ Ph	512
29	3-Me Ph	2,6-Cl ₂ -4-CF ₃ Ph	457
30	4-Br Ph	2,6-Cl ₂ -4-CF ₃ Ph	522
31	4-OMe Ph	2,6-Cl ₂ -4-CF ₃ Ph	473
32	4-pyridyl	2,6-Cl ₂ -4-CF ₃ Ph	444
33	4-NO ₂ Ph	2,6-Cl ₂ -4-CF ₃ Ph	488
34	4-t-butyl Ph	2,6-Cl ₂ -4-CF ₃ Ph	499
35	3-CF ₃ Ph	2,6-Cl ₂ -4-CF ₃ Ph	511
36	4-OCF ₃ Ph	2,6-Cl ₂ -4-CF ₃ Ph	527
37	2-OCF ₃ Ph	2,6-Cl ₂ -4-CF ₃ Ph	527
38	3,4-(OMe) ₂ Ph	2,6-Cl ₂ -4-CF ₃ Ph	503
39	2,4,6-Cl ₃ Ph	2,6-Cl ₂ -4-CF ₃ Ph	546
40	3-Cl-5-CF ₃ -pyrid-2-yl	2,6-Cl ₂ -4-CF ₃ Ph	546
41	cyclopentyl	2,6-Cl ₂ -4-OCF ₃ Ph	451
42	cyclohexyl	2,6-Cl ₂ -4-OCF ₃ Ph	465
43	1,1-Me ₂ -propyl	2,6-Cl ₂ -4-OCF ₃ Ph	453
44	isopropyl	2,6-Cl ₂ -4-OCF ₃ Ph	425
45	1-Me-propyl	2,6-Cl ₂ -4-OCF ₃ Ph	439
46	3-Me-butyl	2,6-Cl ₂ -4-OCF ₃ Ph	453
47	4-Cl benzyl	2,6-Cl ₂ -4-OCF ₃ Ph	507
48	4-OMe benzyl	2,6-Cl ₂ -4-OCF ₃ Ph	503
49	2-Me-propyl	2,6-Cl ₂ -4-OCF ₃ Ph	439
50	2-Me-butyl	2,6-Cl ₂ -4-OCF ₃ Ph	453
51	ethyl	2,6-Cl ₂ -4-OCF ₃ Ph	411

Cpd No.	R1	Q	MS
52	propyl	2,6-Cl ₂ -4-OCF ₃ Ph	425
53	3-Cl-propyl	2,6-Cl ₂ -4-OCF ₃ Ph	459
54	butyl	2,6-Cl ₂ -4-OCF ₃ Ph	439
55	4-t-butyl benzyl	2,6-Cl ₂ -4-OCF ₃ Ph	529
56	CH ₂ CF ₃	2,6-Cl ₂ -4-OCF ₃ Ph	465
57	CH ₂ CHCl ₂	2,6-Cl ₂ -4-OCF ₃ Ph	480
58	2-naphthyl	2,6-Cl ₂ -4-OCF ₃ Ph	509
59	Ph	2,6-Cl ₂ -4-OCF ₃ Ph	459
60	2,5-Cl ₂ Ph	2,6-Cl ₂ -4-OCF ₃ Ph	528
61	2-OMe Ph	2,6-Cl ₂ -4-OCF ₃ Ph	489
62	2-Me Ph	2,6-Cl ₂ -4-OCF ₃ Ph	473
63	3,4-Cl ₂ Ph	2,6-Cl ₂ -4-OCF ₃ Ph	528
64	3-Me Ph	2,6-Cl ₂ -4-OCF ₃ Ph	473
65	4-Br Ph	2,6-Cl ₂ -4-OCF ₃ Ph	538
66	4-OMe Ph	2,6-Cl ₂ -4-OCF ₃ Ph	489
67	4-pyridyl	2,6-Cl ₂ -4-OCF ₃ Ph	460
68	4-NO ₂ Ph	2,6-Cl ₂ -4-OCF ₃ Ph	504
69	5-NO ₂ -pyrid-2-yl	2,6-Cl ₂ -4-OCF ₃ Ph	505
70	3-CF ₃ Ph	2,6-Cl ₂ -4-OCF ₃ Ph	527
71	4-OCF ₃ Ph	2,6-Cl ₂ -4-OCF ₃ Ph	543
72	2-OCF ₃ Ph	2,6-Cl ₂ -4-OCF ₃ Ph	543
73	3,4-(OMe) ₂ Ph	2,6-Cl ₂ -4-OCF ₃ Ph	519
74	2,4,6-Cl ₃ Ph	2,6-Cl ₂ -4-OCF ₃ Ph	562
75	cyclopentyl	2-Cl-4-CF ₃ Ph	400
76	isopropyl	2-Cl-4-CF ₃ Ph	374
77	2-Me-propyl	2-Cl-4-CF ₃ Ph	388
78	3-Me-butyl	2-Cl-4-CF ₃ Ph	402
79	4-Cl benzyl	2-Cl-4-CF ₃ Ph	457

Cpd No.	R1	Q	MS
80	2-Me-propyl	2-Cl-4-CF ₃ Ph	388
81	2-Me-butyl	2-Cl-4-CF ₃ Ph	402
82	decyl	2-Cl-4-CF ₃ Ph	473
83	ethyl	2-Cl-4-CF ₃ Ph	360
84	CH ₂ CH ₂ Ph	2-Cl-4-CF ₃ Ph	436
85	propyl	2-Cl-4-CF ₃ Ph	374
86	3-Cl-propyl	2-Cl-4-CF ₃ Ph	409
87	butyl	2-Cl-4-CF ₃ Ph	388
88	4-t-butyl benzyl	2-Cl-4-CF ₃ Ph	478
89	CH ₂ CF ₃	2-Cl-4-CF ₃ Ph	414
90	2-naphthyl	2-Cl-4-CF ₃ Ph	458
91	Ph	2-Cl-4-CF ₃ Ph	408
92	2,3,4,5,6-F ₅ Ph	2-Cl-4-CF ₃ Ph	498
93	2,5-Cl ₂ Ph	2-Cl-4-CF ₃ Ph	477
94	2-OMe Ph	2-Cl-4-CF ₃ Ph	438
95	2-i-Pr Ph	2-Cl-4-CF ₃ Ph	450
96	2-Me Ph	2-Cl-4-CF ₃ Ph	422
97	3,4-Cl ₂ Ph	2-Cl-4-CF ₃ Ph	477
98	3-Me Ph	2-Cl-4-CF ₃ Ph	422
99	4-Br Ph	2-Cl-4-CF ₃ Ph	487
100	4-OMe Ph	2-Cl-4-CF ₃ Ph	438
101	4-pyridyl	2-Cl-4-CF ₃ Ph	409
102	4-t-butyl Ph	2-Cl-4-CF ₃ Ph	464
103	3-CF ₃ Ph	2-Cl-4-CF ₃ Ph	476
104	4-i-Pr Ph	2-Cl-4-CF ₃ Ph	450
105	4-OCF ₃ Ph	2-Cl-4-CF ₃ Ph	492
106	2-OCF ₃ Ph	2-Cl-4-CF ₃ Ph	492
107	3,4-(OMe) ₂ Ph	2-Cl-4-CF ₃ Ph	468

Cpd No.	R1	Q	MS
108	2,4,6-Cl ₃ Ph	2-Cl-4-CF ₃ Ph	512
109	cyclohexyl	2-Cl-5-CF ₃ Ph	414
110	isopropyl	2-Cl-5-CF ₃ Ph	374
111	2-Me-propyl	2-Cl-5-CF ₃ Ph	388
112	4-Cl benzyl	2-Cl-5-CF ₃ Ph	457
113	propyl	2-Cl-5-CF ₃ Ph	374
114	pentyl	2-Cl-5-CF ₃ Ph	402
115	CH ₂ CF ₃	2-Cl-5-CF ₃ Ph	414
116	2,3,4,5,6-F ₅ Ph	2-Cl-5-CF ₃ Ph	498
117	2,5-Cl ₂ Ph	2-Cl-5-CF ₃ Ph	477
118	2-OMe Ph	2-Cl-5-CF ₃ Ph	438
119	2-i-Pr Ph	2-Cl-5-CF ₃ Ph	450
120	3,4-Cl ₂ Ph	2-Cl-5-CF ₃ Ph	477
121	3-Me Ph	2-Cl-5-CF ₃ Ph	422
122	4-Br Ph	2-Cl-5-CF ₃ Ph	487
123	4-OMe Ph	2-Cl-5-CF ₃ Ph	438
124	4-pyridyl	2-Cl-5-CF ₃ Ph	409
125	4-NO ₂ Ph	2-Cl-5-CF ₃ Ph	453
126	4-t-butyl Ph	2-Cl-5-CF ₃ Ph	464
127	3-CF ₃ Ph	2-Cl-5-CF ₃ Ph	476
128	4-OCF ₃ Ph	2-Cl-5-CF ₃ Ph	492
129	2-OCF ₃ Ph	2-Cl-5-CF ₃ Ph	492
130	3,4-(OMe) ₂ Ph	2-Cl-5-CF ₃ Ph	468
131	cyclohexyl	2,4,6-Cl ₃ Ph	415
132	isopropyl	2,4,6-Cl ₃ Ph	375
133	benzyl	2,4,6-Cl ₃ Ph	423
134	4-Cl benzyl	2,4,6-Cl ₃ Ph	458
135	2-Me-butyl	2,4,6-Cl ₃ Ph	403

Cpd No.	R1	Q	MS
136	ethyl	2,4,6-Cl ₃ Ph	361
137	propyl	2,4,6-Cl ₃ Ph	375
138	pentyl	2,4,6-Cl ₃ Ph	403
139	hexyl	2,4,6-Cl ₃ Ph	417
140	CH ₂ CF ₃	2,4,6-Cl ₃ Ph	415
141	CH ₂ CHCl ₂	2,4,6-Cl ₃ Ph	430
142	2-naphthyl	2,4,6-Cl ₃ Ph	459
143	2-OMe Ph	2,4,6-Cl ₃ Ph	439
144	2-iPr Ph	2,4,6-Cl ₃ Ph	451
145	3,4-Cl ₂ Ph	2,4,6-Cl ₃ Ph	478
146	4-Br Ph	2,4,6-Cl ₃ Ph	488
147	4-OMe Ph	2,4,6-Cl ₃ Ph	439
148	4-OCF ₃ Ph	2,4,6-Cl ₃ Ph	493
149	isopropyl	2-Br-4,6-Cl ₂ Ph	420
150	3-Me-butyl	2-Br-4,6-Cl ₂ Ph	448
151	4-Cl benzyl	2-Br-4,6-Cl ₂ Ph	502
152	2-Me-butyl	2-Br-4,6-Cl ₂ Ph	448
153	ethyl	2-Br-4,6-Cl ₂ Ph	406
154	CH ₂ CH ₂ Ph	2-Br-4,6-Cl ₂ Ph	482
155	propyl	2-Br-4,6-Cl ₂ Ph	420
156	3-Cl-propyl	2-Br-4,6-Cl ₂ Ph	454
157	CH ₂ CF ₃	2-Br-4,6-Cl ₂ Ph	460
158	2-naphthyl	2-Br-4,6-Cl ₂ Ph	504
159	Ph	2-Br-4,6-Cl ₂ Ph	454
160	2,5-Cl ₂ Ph	2-Br-4,6-Cl ₂ Ph	523
161	2-iPr Ph	2-Br-4,6-Cl ₂ Ph	496
162	2-Me Ph	2-Br-4,6-Cl ₂ Ph	468
163	3,4-Cl ₂ Ph	2-Br-4,6-Cl ₂ Ph	523

Cpd No.	R1	Q	MS
164	3-Me Ph	2-Br-4,6-Cl ₂ Ph	468
165	4-Br Ph	2-Br-4,6-Cl ₂ Ph	533
166	4-OMe Ph	2-Br-4,6-Cl ₂ Ph	484
167	4- <i>t</i> -butyl Ph	2-Br-4,6-Cl ₂ Ph	510
168	4-OCF ₃ Ph	2-Br-4,6-Cl ₂ Ph	538
169	2,4,6-Cl ₃ Ph	2-Br-4,6-Cl ₂ Ph	557
170	cyclopentyl	2,6-Cl ₂ -4-Br Ph	446
171	cyclohexyl	2,6-Cl ₂ -4-Br Ph	460
172	1,1-Me ₂ -propyl	2,6-Cl ₂ -4-Br Ph	448
173	isopropyl	2,6-Cl ₂ -4-Br Ph	420
174	1-Me-propyl	2,6-Cl ₂ -4-Br Ph	434
175	3-Me-butyl	2,6-Cl ₂ -4-Br Ph	448
176	4-Cl benzyl	2,6-Cl ₂ -4-Br Ph	502
177	4-OMe benzyl	2,6-Cl ₂ -4-Br Ph	498
178	2-Me-butyl	2,6-Cl ₂ -4-Br Ph	448
179	ethyl	2,6-Cl ₂ -4-Br Ph	406
180	propyl	2,6-Cl ₂ -4-Br Ph	420
181	butyl	2,6-Cl ₂ -4-Br Ph	434
182	hexyl	2,6-Cl ₂ -4-Br Ph	462
183	CH ₂ CF ₃	2,6-Cl ₂ -4-Br Ph	460
184	CH ₂ CHCl ₂	2,6-Cl ₂ -4-Br Ph	475

Example 2

A solution of 5-amino-1-(2,6-dichloro-4-trifluoromethylphenyl)-3-cyano-4-methylthiomethylpyrazole (1.0g) in methanol was cooled to 0°C, then treated with sulphuric acid/isopropanol catalyst (1ml), followed by hydrogen peroxide (0.31g of 30% w/w). The mixture was stirred overnight, quenched with water, the solid collected and washed with methyl *t*-butyl ether to give 5-amino-1-(2,6-dichloro-4-

trifluoromethylphenyl)-3-cyano-4-methylsulphinylmethylpyrazole (Compound 185, 0.63g), MS 396. 1-(2,6-Dichloro-4-trifluoromethylphenyl)-3-cyano-5-methylamino-4-methylsulphinylmethylpyrazole (Compound 268) was prepared in a similar manner.

The following compounds of formula (I), shown in Table 2 in which R² is amino and n is 1 were prepared in a similar manner but replacing the methanol with trifluoroacetic acid and without the sulphuric acid/isopropanol catalyst, and purified by silica gel chromatography using a heptane/ethyl acetate/methanol gradient.

Table 2

Cpd No.	R1	Q	MS
186	cyclopentyl	2,6-Cl ₂ -4-CF ₃ Ph	451
187	cyclohexyl	2,6-Cl ₂ -4-CF ₃ Ph	465
188	1,1-Me ₂ -propyl	2,6-Cl ₂ -4-CF ₃ Ph	453
189	isopropyl	2,6-Cl ₂ -4-CF ₃ Ph	425
190	1-Me-propyl	2,6-Cl ₂ -4-CF ₃ Ph	439
191	benzyl	2,6-Cl ₂ -4-CF ₃ Ph	473
192	3-Me-butyl	2,6-Cl ₂ -4-CF ₃ Ph	453
193	4-OMe benzyl	2,6-Cl ₂ -4-CF ₃ Ph	503
194	2-Me-propyl	2,6-Cl ₂ -4-CF ₃ Ph	439
195	2-Me-butyl	2,6-Cl ₂ -4-CF ₃ Ph	453
196	ethyl	2,6-Cl ₂ -4-CF ₃ Ph	411
197	propyl	2,6-Cl ₂ -4-CF ₃ Ph	425
198	hexyl	2,6-Cl ₂ -4-CF ₃ Ph	467
199	4-t-Bu benzyl	2,6-Cl ₂ -4-CF ₃ Ph	529
200	isopropyl	2,6-Cl ₂ -4-OCF ₃ Ph	441
201	1-Me-propyl	2,6-Cl ₂ -4-OCF ₃ Ph	455
202	benzyl	2,6-Cl ₂ -4-OCF ₃ Ph	489
203	4-OMe benzyl	2,6-Cl ₂ -4-OCF ₃ Ph	519
204	2-Me-propyl	2,6-Cl ₂ -4-OCF ₃ Ph	455
205	2-Me-butyl	2,6-Cl ₂ -4-OCF ₃ Ph	469

Cpd No.	R1	Q	MS
206	ethyl	2,6-Cl ₂ -4-OCF ₃ Ph	427
207	propyl	2,6-Cl ₂ -4-OCF ₃ Ph	441
208	cyclopentyl	2-Cl-4-CF ₃ Ph	416
209	4-Cl benzyl	2-Cl-4-CF ₃ Ph	473
210	propyl	2-Cl-4-CF ₃ Ph	390
211	4-Me benzyl	2-Cl-4-CF ₃ Ph	452
212	4-t-Bu benzyl	2-Cl-4-CF ₃ Ph	494
213	benzyl	2-Cl-5-CF ₃ Ph	438
214	decyl	2-Cl-5-CF ₃ Ph	489
215	4-Me benzyl	2-Cl-5-CF ₃ Ph	452
216	2-OMe Ph	2-Cl-5-CF ₃ Ph	454
217	3,4-Cl ₂ Ph	2-Cl-5-CF ₃ Ph	(a)
218	4-OCF ₃ Ph	2-Cl-5-CF ₃ Ph	(a)
219	3-Me-butyl	2,4,6-Cl ₃ Ph	419
220	ethyl	2,4,6-Cl ₃ Ph	377
221	butyl	2,4,6-Cl ₃ Ph	405
222	4-t-Bu benzyl	2,4,6-Cl ₃ Ph	495
223	isopropyl	2-Br-4,6-Cl ₂ Ph	436
224	propyl	2-Br-4,6-Cl ₂ Ph	436
225	cyclohexyl	2,6-Cl ₂ -4-Br Ph	476
226	1,1-dimethylpropyl	2,6-Cl ₂ -4-Br Ph	464
227	isopropyl	2,6-Cl ₂ -4-Br Ph	436
228	2-Me-propyl	2,6-Cl ₂ -4-Br Ph	450
229	decyl	2,6-Cl ₂ -4-Br Ph	534
230	propyl	2,6-Cl ₂ -4-Br Ph	436
231	butyl	2,6-Cl ₂ -4-Br Ph	450

Note: (a) = not observed.

By proceeding in a similar manner the following compounds of formula (I), shown in Table 2 in which R² is amino and n is 2 were also prepared.

Table 3

Cpd No.	R1	Q	MS
232	methyl	2,6-Cl ₂ -4-CF ₃ Ph	413
233	isopropyl	2,6-Cl ₂ -4-CF ₃ Ph	441
234	benzyl	2,6-Cl ₂ -4-CF ₃ Ph	(a)
235	ethyl	2,6-Cl ₂ -4-CF ₃ Ph	427
236	propyl	2,6-Cl ₂ -4-CF ₃ Ph	441
237	3-Cl-propyl	2,6-Cl ₂ -4-CF ₃ Ph	475
238	butyl	2,6-Cl ₂ -4-CF ₃ Ph	455
239	hexyl	2,6-Cl ₂ -4-CF ₃ Ph	483
240	Ph	2,6-Cl ₂ -4-CF ₃ Ph	475
241	4-OMe Ph	2,6-Cl ₂ -4-CF ₃ Ph	505
242	4-tBu Ph	2,6-Cl ₂ -4-CF ₃ Ph	531
243	3-CF ₃ Ph	2,6-Cl ₂ -4-CF ₃ Ph	543
244	4-iPr Ph	2,6-Cl ₂ -4-CF ₃ Ph	517
245	4-OCF ₃ Ph	2,6-Cl ₂ -4-CF ₃ Ph	559
246	2-OCF ₃ Ph	2,6-Cl ₂ -4-CF ₃ Ph	559
247	cyclopentyl	2,6-Cl ₂ -4-OCF ₃ Ph	483
248	benzyl	2,6-Cl ₂ -4-OCF ₃ Ph	505
249	4-Cl benzyl	2,6-Cl ₂ -4-OCF ₃ Ph	539
250	2-Me-propyl	2,6-Cl ₂ -4-OCF ₃ Ph	471
251	2-Me-butyl	2,6-Cl ₂ -4-OCF ₃ Ph	485
252	decyl	2,6-Cl ₂ -4-OCF ₃ Ph	555
253	hexyl	2,6-Cl ₂ -4-OCF ₃ Ph	499
254	Ph	2,6-Cl ₂ -4-OCF ₃ Ph	491
255	2-iPr Ph	2,6-Cl ₂ -4-OCF ₃ Ph	533

Cpd No.	R1	Q	MS
256	3-Me-butyl	2-Cl-4-CF ₃ Ph	434
257	4-t-Bu Ph	2-Cl-4-CF ₃ Ph	496
258	isopropyl	2-Cl-5-CF ₃ Ph	406
259	4-Cl benzyl	2-Cl-5-CF ₃ Ph	489
260	isopropyl	2,4,6-Cl ₃ Ph	407
261	4-iPr Ph	2-Br-4,6-Cl ₂ Ph	528
262	2-OCF ₃ Ph	2-Br-4,6-Cl ₂ Ph	570
263	4-Cl benzyl	2,6-Cl ₂ -4-CF ₃ Ph	498
264	propyl	2,6-Cl ₂ -4-CF ₃ Ph	416
265	propyl	2-Br-4,6-Cl ₂ Ph	452
266	CH ₂ CHCl ₂	2,6-Cl ₂ -4-CF ₃ Ph	(a)
267	4-Cl benzyl	2,6-Cl ₂ -4-Br Ph	534

Note: (a) = not observed.

Example 3

Sodium borohydride (420mg) was added portionwise to a solution of 1-(2,6-dichloro-4-trifluoromethylphenyl)-3-cyano-5-ethoxycarbonylamino-4-methylthiomethylpyrazole (854mg) in methanol. The mixture was evaporated, diluted with dichloromethane and water, and the organic phase dried (magnesium sulphate) and evaporated to give 1-(2,6-dichloro-4-trifluoromethylphenyl)-3-cyano-5-methylamino-4-methylthiomethylpyrazole.

Example 4

A solution of 5-amino-1-(2,6-dichloro-4-trifluoromethylphenyl)-3-cyano-4-methylthiomethylpyrazole (801mg) in triethyl orthoformate was heated to 80°C, concentrated hydrochloric acid (2 drops) added, and the mixture heated until it had a pH of 6. Evaporation then gave 1-(2,6-dichloro-4-trifluoromethylphenyl)-3-cyano-5-ethoxymethyleneamino-4-methylthiomethylpyrazole (Compound 269, 875mg).

The term "compound of the invention" as used hereinafter embraces a 4-thiomethylpyrazole of formula (I) as defined above and a pesticidally acceptable salt thereof.

One aspect of the present invention as defined above is a method for the control of pests at a locus. The locus includes, for example, the pest itself, the place (plant, field, forest, orchard, waterway, soil, plant product, or the like) where the pest resides or feeds, or a place susceptible to future infestation by the pest. The compound of the invention may therefore be applied directly to the pest, to the place where the pest resides or feeds, or to the place susceptible to future infestation by the pest.

As is evident from the foregoing pesticidal uses, the present invention provides pesticidally active compounds and methods of use of said compounds for the control of a number of pest species which includes: arthropods, especially insects or mites, or plant nematodes. The compound of the invention may thus be advantageously employed in practical uses, for example, in agricultural or horticultural crops, in forestry, in veterinary medicine or livestock husbandry, or in public health.

The compounds of the invention may be used for example in the following applications and on the following pests:

For the control of soil insects, such as corn rootworm, termites (especially for protection of structures), root maggots, wireworms, root weevils, stalkborers, cutworms, root aphids, or grubs. They may also be used to provide activity against plant pathogenic nematodes, such as root-knot, cyst, dagger, lesion, or stem or bulb nematodes, or against mites. For the control of soil pests, for example corn rootworm, the compounds are advantageously applied to or incorporated at an effective rate into the soil in which crops are planted or to be planted or to the seeds or growing plant roots.

In the area of public health, the compounds are especially useful in the control of many insects, especially filth flies or other Dipteran pests, such as houseflies, stableflies, soldierflies, hornflies, deerflies, horseflies, midges, punkies, blackflies, or mosquitoes.

In the protection of stored products, for example cereals, including grain or flour, groundnuts, animal feedstuffs, timber or household goods, e.g. carpets and textiles, compounds of the invention are useful against attack by arthropods, more especially beetles, including weevils, moths or mites, for example *Ephestia* spp. (flour moths), *Anthrenus* spp. (carpet beetles), *Tribolium* spp. (flour beetles), *Sitophilus* spp. (grain weevils) or *Acarus* spp. (mites).

In the control of cockroaches, ants or termites or similar arthropod pests in infested domestic or industrial premises or in the control of mosquito larvae in waterways, wells, reservoirs or other running or standing water.

For the treatment of foundations, structures or soil in the prevention of the attack on building by termites, for example, *Reticulitermes* spp., *Heterotermes* spp., *Coptotermes* spp..

In agriculture against adults, larvae and eggs of Lepidoptera (butterflies and moths), e.g. *Heliothis* spp. such as *Heliothis virescens* (tobacco budworm), *Heliothis armigera* and *Heliothis zea*. Against adults and larvae of Coleoptera (beetles) e.g. *Anthonomus* spp. e.g. *grandis* (cotton boll weevil), *Leptinotarsa decemlineata* (Colorado potato beetle), *Diabrotica* spp. (corn rootworms). Against Heteroptera (Hemiptera and Homoptera) e.g. *Psylla* spp., *Bemisia* spp., *Trialeurodes* spp., *Aphis* spp., *Myzus* spp., *Megoura viciae*, *Phylloxera* spp., *Nephotettix* spp. (rice leaf hoppers), *Nilaparvata* spp..

Against Diptera e.g. *Musca* spp.. Against Thysanoptera such as *Thrips tabaci*. Against Orthoptera such as *Locusta* and *Schistocerca* spp., (locusts and crickets) e.g. *Gryllus* spp., and *Acheta* spp. for example, *Blatta orientalis*, *Periplaneta americana*, *Blatella germanica*, *Locusta migratoria migratorioides*, and *Schistocerca gregaria*. Against Collembola e.g. *Periplaneta* spp. and *Blatella* spp. (roaches).

Against arthropods of agricultural significance such as Acari (mites) e.g. *Tetranychus* spp., and *Panonychus* spp..

Against nematodes which attack plants or trees of importance to agriculture, forestry or horticulture either directly or by spreading bacterial, viral, mycoplasma or fungal diseases of the plants. For example root-knot nematodes such as *Meloidogyne* spp. (e.g. *M. incognita*).

In the field of veterinary medicine or livestock husbandry or in the maintenance of public health against arthropods which are parasitic internally or externally upon vertebrates, particularly warm-blooded vertebrates, for example domestic animals, e.g. cattle, sheep, goats, equines, swine, poultry, dogs or cats, for example Acarina, including ticks (e.g. *Ixodes* spp., *Boophilus* spp. e.g. *Boophilus microplus*, *Rhipicephalus* spp. e.g.

Rhipicephalus appendiculatus *Ornithodoros* spp. (e.g. *Ornithodoros moubata*) and mites (e.g. *Damalinia* spp.); Diptera (e.g. *Aedes* spp., *Anopheles* spp., *Musca* spp.,

Hypoderma spp.); Hemiptera.; Dictyoptera (e.g. *Periplaneta* spp., *Blatella* spp.);

Hymenoptera; for example against infections of the gastro-intestinal tract caused by parasitic nematode worms, for example members of the family *Trichostrongylidae*.

In practical use of compounds of formula (I) or compositions hereinafter described for the control of pests, like arthropods, especially insects or mites, or nematode pests of plants, a method, for example, comprises applying to the plants or to the medium in

which they grow an effective amount of a compound of the invention. For such a method, the active compound is generally applied to the locus in which the arthropod or nematode infestation is to be controlled at an effective rate in the range of about 2g to about 5kg of the active compound per hectare of locus treated. Under ideal conditions, depending on the pest to be controlled, a lower rate may offer adequate protection. On the other hand, adverse weather conditions, resistance of the pest or other factors may require that the active ingredient be used at higher rates. The optimum rate depends usually upon a number of factors, for example, the type of pest being controlled, the type or the growth stage of the infested plant, the row spacing or also the method of application. Preferably an effective rate range of the active compound is from about 10g/ha to about 400g/ha, more preferably from about 50g/ha to about 200 g/ha. When a pest is soil-borne, the active compound generally in a formulated composition, is distributed evenly over the area to be treated (ie, for example broadcast or band treatment) in any convenient manner and is applied at rates from about 10g/ha to about 400g ai/ha, preferably from about 50g/ha to about 200 g ai/ha. When applied as a root dip to seedlings or drip irrigation to plants the liquid solution or suspension contains from about 0.075 to about 1000 mg ai/l, preferably from about 25 to about 200 mg ai/l. Application may be made, if desired, to the field or crop-growing area generally or in close proximity to the seed or plant to be protected from attack. The active component can be washed into the soil by spraying with water over the area or can be left to the natural action of rainfall. During or after application, the formulated compound can, if desired, be distributed mechanically in the soil, for example by ploughing, disking, or use of drag chains. Application can be prior to planting, at planting, after planting but before sprouting has taken place, or after sprouting. Accordingly, in a further aspect of the invention there is provided a seed, treated or coated with a compound of the formula (I) or a composition as described hereinafter. The compound of the invention and methods of control of pests therewith are of particular value in the protection of field, forage, plantation, glasshouse, orchard or vineyard crops, of ornamentals, or of plantation or forest trees, for example: cereals (such as wheat or rice), cotton, vegetables (such as peppers), field crops (such as sugar beets, soybeans or oil seed rape), grassland or forage crops (such as maize or sorghum), orchards or groves (such as of stone or pit fruit or citrus), ornamental plants, flowers or vegetables or shrubs under glass or in gardens or parks, or forest trees (both deciduous and evergreen) in forests, plantations or nurseries.

They are also valuable in the protection of timber (standing, felled, converted, stored or structural) from attack, for example, by sawflies or beetles or termites.

They have applications in the protection of stored products such as grains, fruits, nuts, spices or tobacco, whether whole, milled or compounded into products, from moth, beetle, mite or grain weevil attack. Also protected are stored animal products such as skins, hair, wool or feathers in natural or converted form (e.g. as carpets or textiles) from moth or beetle attack as well as stored meat, fish or grains from beetle, mite or fly attack.

Additionally, the compound of the invention and methods of use thereof are of particular value in the control of arthropods or helminths which are injurious to, or spread or act as vectors of diseases domestic animals, for example those hereinbefore mentioned, and more especially in the control of ticks, mites, lice, fleas, midges, or biting, nuisance or myiasis flies. The compounds of the invention are particularly useful in controlling arthropods or helminths which are present inside domestic host animals or which feed in or on the skin or suck the blood of the animal, for which purpose they may be administered orally, parenterally, percutaneously or topically.

Accordingly, in a further aspect of the invention there is provided the use of a compound of the formula (I) or a composition hereinafter described for preparing a veterinary medicine.

The compositions hereinafter described for application to growing crops or crop growing loci or as a seed dressing may, in general, alternatively be employed in the protection of stored products, household goods, property or areas of the general environment.

Suitable means of applying the compounds of the invention include:

to growing crops as foliar sprays (for example as an in-furrow spray), dusts, granules, fogs or foams or also as suspensions of finely divided or encapsulated compositions as soil or root treatments by liquid drenches, dusts, granules, smokes or foams; to seeds of crops via application as seed dressings by liquid slurries or dusts; to animals infested by or exposed to infestation by arthropods or helminths, by parenteral, oral or topical application of compositions in which the active ingredient exhibits an immediate and/or prolonged action over a period of time against the arthropods or helminths, for example by incorporation in feed or suitable orally-ingestible pharmaceutical formulations, edible baits, salt licks, dietary supplements, pour-on formulations, sprays, baths, dips, showers, jets, dusts, greases, shampoos, creams, wax smears or livestock self-treatment systems;

to the environment in general or to specific locations where pests may lurk, including stored products, timber, household goods, or domestic or industrial premises, as sprays, fogs, dusts, smokes, wax-smears, lacquers, granules or baits, or in tricklefeeds to waterways, wells, reservoirs or other running or standing water.

According to a further feature of the present invention there is provided a pesticidal composition comprising one or more compounds of the invention as defined above, in association with, and preferably homogeneously dispersed in one or more compatible agriculturally acceptable diluents or carriers and/or surface active agents [i.e. diluents or carriers and/or surface active agents of the type generally accepted in the art as being suitable for use in herbicidal compositions and which are compatible with compounds of the invention], and the use therefor for controlling pests.

In practice, the compounds of the invention most frequently form parts of compositions. These compositions can be employed to control arthropods, especially insects, or plant nematodes or mites. The compositions may be of any type known in the art suitable for application to the desired pest in any premises or indoor or outdoor area. These compositions contain at least one compound of the invention as the active ingredient in combination or association with one or more other compatible components which are for example, solid or liquid carriers or diluents, adjuvants, surface-active-agents, or the like appropriate for the intended use and which are agronomically or medicinally acceptable. These compositions, which may be prepared by any manner known in the art, likewise form a part of this invention.

These compositions may also contain other kinds of ingredients such as protective colloids, adhesives, thickeners, thixotropic agents, penetrating agents, spray oils (especially for acaridical use), stabilizers, preservative agents (especially mold preservatives), sequestering agents, or the like, as well as other known active ingredients with pesticidal properties (particularly insecticidal, miticidal, nematocidal, or fungicidal) or with properties regulating the growth of plants. More generally, the compounds employed in the invention may be combined with all the solid or liquid additives corresponding to the usual techniques of formulation.

Examples of other pesticidally-active compounds which may be included in, or used in conjunction with the compositions of the present invention are: acephate, chlorpyrifos, demeton-S-methyl, disulfoton, ethoprophos, fenitrothion, fenamiphos, fonofos, isazophos, isofenphos, malathion, monocrotophos, parathion, phorate, phosalone, pirimiphos-

methyl, terbufos, triazophos, cyfluthrin, cypermethrin, deltamethrin, fenpropathrin, fenvalerate, permethrin, tefluthrin, aldicarb, carbosulfan, methomyl, oxamyl, pirimicarb, bendiocarb, teflubenzuron, dicofol, endosulfan, lindane, benzoximate, cartap, cyhexatin, tetradifon, avermectins, ivermectins, milbemycins, thiophanate, trichlorfon, dichlorvos, diaveridine or dimetriadazole.

Compositions, suitable for applications in agriculture, horticulture, or the like include formulations suitable for use as, for example, sprays, dusts, granules, fogs, foams, emulsions, or the like.

The effective use doses of the compounds employed in the invention can vary within wide limits, particularly depending on the nature of the pest to be eliminated or degree of infestation, for example, of crops with these pests. In general, the compositions according to the invention usually contain about 0.05 to about 95% (by weight) of one or more active ingredients according to the invention, about 1 to about 95% of one or more solid or liquid carriers and, optionally, about 0.1 to about 50% of one or more other compatible components, such as surface-active agents or the like.

In the present account, the term "carrier" denotes an organic or inorganic ingredient, natural or synthetic, with which the active ingredient is combined to facilitate its application, for example, to the plant, to seeds or to the soil. This carrier is therefore generally inert and it must be acceptable (for example, agronomically acceptable, particularly to the treated plant).

The carrier may be a solid, for example, clays, natural or synthetic silicates, silica, resins, waxes, solid fertilizers (for example ammonium salts), ground natural minerals, such as kaolins, clays, talc, chalk, quartz, attapulgite, montmorillonite, bentonite or diatomaceous earth, or ground synthetic minerals, such as silica, alumina, or silicates especially aluminium or magnesium silicates. As solid carriers for granules the following are suitable: crushed or fractionated natural rocks such as calcite, marble, pumice, sepiolite and dolomite; synthetic granules of inorganic or organic meals; granules of organic material such as sawdust, coconut shells, corn cobs, corn husks or tobacco stalks; kieselguhr, tricalcium phosphate, powdered cork, or absorbent carbon black; water soluble polymers, resins, waxes; or solid fertilizers. Such solid compositions may, if desired, contain one or more compatible wetting, dispersing, emulsifying or colouring agents which, when solid, may also serve as a diluent.

The carrier may also be liquid, for example: water; alcohols, particularly butanol or glycol, as well as their ethers or esters, particularly methylglycol acetate; ketones,

particularly acetone, cyclohexanone, methylethyl ketone, methylisobutylketone, or isophorone; petroleum fractions such as paraffinic or aromatic hydrocarbons, particularly xylenes or alkyl naphthalenes; mineral or vegetable oils; aliphatic chlorinated hydrocarbons, particularly trichloroethane or methylene chloride; aromatic chlorinated hydrocarbons, particularly chlorobenzenes; water-soluble or strongly polar solvents such as dimethylformamide, dimethyl sulphoxide, or N-methylpyrrolidone; liquefied gases; or the like or a mixture thereof.

The surface-active agent may be an emulsifying agent, dispersing agent or wetting agent of the ionic or non-ionic type or a mixture of such surface-active agents.

Amongst these are e.g., salts of polyacrylic acids, salts of lignosulphonic acids, salts of phenolsulphonic or naphthalenesulphonic acids, polycondensates of ethylene oxide with fatty alcohols or fatty acids or fatty esters or fatty amines, substituted phenols (particularly alkylphenols or arylphenols), salts of sulphosuccinic acid esters, taurine derivatives (particularly alkyltaurates), phosphoric esters of alcohols or of polycondensates of ethylene oxide with phenols, esters of fatty acids with polyols, or sulphate, sulphonate or phosphate functional derivatives of the above compounds. The presence of at least one surface-active agent is generally essential when the active ingredient and/or the inert carrier are only slightly water soluble or are not water soluble and the carrier agent of the composition for application is water.

Compositions of the invention may further contain other additives such as adhesives or colorants. Adhesives such as carboxymethylcellulose or natural or synthetic polymers in the form of powders, granules or lattices, such as arabic gum, polyvinyl alcohol or polyvinyl acetate, natural phospholipids, such as cephalins or lecithins, or synthetic phospholipids can be used in the formulations. It is possible to use colorants such as inorganic pigments, for example: iron oxides, titanium oxides or Prussian Blue; organic dyestuffs, such as alizarin dyestuffs, azo dyestuffs or metal phthalocyanine dyestuffs; or trace nutrients such as salts of iron, manganese, boron, copper, cobalt, molybdenum or zinc.

For their agricultural application, the compounds of the invention are therefore generally in the form of compositions, which are in various solid or liquid forms.

Solid forms of compositions which can be used are dusting powders (with a content of the compound of the invention, ranging up to 80%), wettable powders or granules (including water dispersible granules), particularly those obtained by extrusion, compacting, impregnation of a granular carrier, or granulation starting from a powder

(the content of the compound of the invention, in these wettable powders or granules being between about 0.5 and about 80%). Solid homogenous or heterogenous compositions containing one or more compounds of the invention, for example granules, pellets, briquettes or capsules, may be used to treat standing or running water over a period of time. A similar effect may be achieved using trickle or intermittent feeds of water dispersible concentrates as described herein.

Liquid compositions, for example, include aqueous or non-aqueous solutions or suspensions (such as emulsifiable concentrates, emulsions, flowables, dispersions, or solutions) or aerosols. Liquid compositions also include, in particular, emulsifiable concentrates, dispersions, emulsions, flowables, aerosols, wettable powders (or powder for spraying), dry flowables or pastes as forms of compositions which are liquid or intended to form liquid compositions when applied, for example as aqueous sprays (including low and ultra-low volume) or as fogs or aerosols.

Liquid compositions, for example, in the form of emulsifiable or soluble concentrates most frequently comprise about 5 to about 80% by weight of the active ingredient, while the emulsions or solutions which are ready for application contain, in their case, about 0.01 to about 20% of the active ingredient. Besides the solvent, the emulsifiable or soluble concentrates may contain, when required, about 2 to about 50% of suitable additives, such as stabilizers, surface-active agents, penetrating agents, corrosion inhibitors, colorants or adhesives. Emulsions of any required concentration, which are particularly suitable for application, for example, to plants, may be obtained from these concentrates by dilution with water. These compositions are included within the scope of the compositions which may be employed in the present invention. The emulsions may be in the form of water-in-oil or oil-in-water type and they may have a thick consistency.

The liquid compositions of this invention may, in addition to normal agricultural use applications be used for example to treat substrates or sites infested or liable to infestation by arthropods (or other pests controlled by compounds of this invention) including premises, outdoor or indoor storage or processing areas, containers or equipment or standing or running water.

All these aqueous dispersions or emulsions or spraying mixtures can be applied, for example, to crops by any suitable means, chiefly by spraying, at rates which are generally of the order of about 100 to about 1,200 liters of spraying mixture per hectare, but may be higher or lower (eg. low or ultra-low volume) depending upon the

need or application technique. The compound or compositions according to the invention are conveniently applied to vegetation and in particular to roots or leaves having pests to be eliminated. Another method of application of the compounds or compositions according to the invention is by chemigation, that is to say, the addition of a formulation containing the active ingredient to irrigation water. This irrigation may be sprinkler irrigation for foliar pesticides or it can be ground irrigation or underground irrigation for soil or for systemic pesticides.

The concentrated suspensions, which can be applied by spraying, are prepared so as to produce a stable fluid product which does not settle (fine grinding) and usually contain from about 10 to about 75% by weight of active ingredient, from about 0.5 to about 30% of surface-active agents, from about 0.1 to about 10% of thixotropic agents, from about 0 to about 30% of suitable additives, such as anti-foaming agents, corrosion inhibitors, stabilizers, penetrating agents, adhesives and, as the carrier, water or an organic liquid in which the active ingredient is poorly soluble or insoluble. Some organic solids or inorganic salts may be dissolved in the carrier to help prevent settling or as antifreezes for water.

The wettable powers (or powder for spraying) are usually prepared so that they contain from about 10 to about 80% by weight of active ingredient, from about 20 to about 90% of a solid carrier, from about 0 to about 5% of a wetting agent, from about 3 to about 10% of a dispersing agent and, when necessary, from about 0 to about 80% of one or more stabilizers and/or other additives, such as penetrating agents, adhesives, anti-caking agents, colorants, or the like. To obtain these wettable powders, the active ingredient is thoroughly mixed in a suitable blender with additional substances which may be impregnated on the porous filler and is ground using a mill or other suitable grinder. This produces wettable powders, the wettability and the suspendability of which are advantageous. They may be suspended in water to give any desired concentration and this suspension can be employed very advantageously in particular for application to plant foliage.

The "water dispersible granules (WG)" (granules which are readily dispersible in water) have compositions which are substantially close to that of the wettable powders. They may be prepared by granulation of formulations described for the wettable powders, either by a wet route (contacting finely divided active ingredient with the inert filler and a little water, e.g. 1 to 20% by weight, or with an aqueous solution of a dispersing

agent or binder, followed by drying and screening), or by a dry route (compacting followed by grinding and screening).

The rates and concentrations of the formulated compositions may vary according to the method of application or the nature of the compositions or use thereof. Generally speaking, the compositions for application to control arthropod or plant nematode pests usually contain from about 0.00001% to about 95%, more particularly from about 0.0005% to about 50% by weight of one or more compounds of the invention, or of total active ingredients (that is to say the compounds of the invention, together with: other substances toxic to arthropods or plant nematodes, synergists, trace elements or stabilizers). The actual compositions employed and their rate of application will be selected to achieve the desired effect(s) by the farmer, livestock producer, medical or veterinary practitioner, pest control operator or other person skilled in the art.

Solid or liquid compositions for application topically to animals, timber, stored products or household goods usually contain from about 0.00005% to about 90%, more particularly from about 0.001% to about 10%, by weight of one or more compounds of the invention. For administration to animals orally or parenterally, including percutaneously solid or liquid compositions, these normally contain from about 0.1% to about 90% by weight of one or more compounds of the invention. Medicated feedstuffs normally contain from about 0.001% to about 3% by weight of one or more compounds of the invention. Concentrates or supplements for mixing with feedstuffs normally contain from about 5% to about 90%, preferably from about 5% to about 50%, by weight of one or more compounds of the invention. Mineral salt licks normally contain from about 0.1% to about 10% by weight of one or more compounds of formula (I) or pesticidally acceptable salts thereof.

Dusts or liquid compositions for application to livestock, goods, premises or outdoor areas may contain from about 0.0001% to about 15%, more especially from about 0.005% to about 2.0%, by weight, of one or more compounds of the invention.

Suitable concentrations in treated waters are between about 0.0001 ppm and about 20 ppm, more particularly about 0.001 ppm to about 5.0 ppm, of one or more compounds of the invention, and may be used therapeutically in fish farming with appropriate exposure times. Edible baits may contain from about 0.01% to about 5%, preferably from about 0.01% to about 1.0%, by weight, of one or more compounds of the invention.

When administered to vertebrates parenterally, orally or by percutaneous or other means, the dosage of compounds of the invention, will depend upon the species, age, or health of the vertebrate and upon the nature and degree of its actual or potential infestation by arthropod or helminth pests. A single dose of about 0.1 to about 100 mg, preferably about 2.0 to about 20.0 mg, per kg body weight of the animal or doses of about 0.01 to about 20.0 mg, preferably about 0.1 to about 5.0 mg, per kg body weight of the animal per day, for sustained medication, are generally suitable by oral or parenteral administration. By use of sustained release formulations or devices, the daily doses required over a period of months may be combined and administered to animals on a single occasion.

The following composition EXAMPLES 2A - 2M illustrate compositions for use against arthropods, especially mites or insects, or plant nematodes, which comprise, as active ingredient, compounds of the invention, such as those described in preparative examples. The compositions described in EXAMPLES 2A - 2M can each be diluted to give a sprayable composition at concentrations suitable for use in the field. Generic chemical descriptions of the ingredients (for which all of the following percentages are in weight percent), used in the composition EXAMPLES 2A - 2M exemplified below, are as follows:

Trade Name	Chemical Description
Ethylan BCP	Nonylphenol ethylene oxide condensate
Soprophor BSU	Tristyrylphenol ethylene oxide condensate
Arylan CA	A 70% w/v solution of calcium dodecylbenzenesulfonate
Solvesso 150	Light C ₁₀ aromatic solvent
Arylan S	Sodium dodecylbenzenesulfonate
Darvan NO ₂	Sodium lignosulphonate
Celite PF	Synthetic magnesium silicate carrier
Sopropon T36	Sodium salts of polycarboxylic acids
Rhodigel 23	Polysaccharide xanthan gum
Bentone 38	Organic derivative of magnesium montmorillonite
Aerosil	Microfine silicon dioxide
EXAMPLE 2A	

A water soluble concentrate is prepared with the composition as follows:

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Active ingredient	7%
Ethylan BCP	10%
N-methylpyrrolidone	83%

To a solution of Ethylan BCP dissolved in a portion of N-methylpyrrolidone is added the active ingredient with heating and stirring until dissolved. The resulting solution is made up to volume with the remainder of the solvent.

EXAMPLE 2B

An emulsifiable concentrate (EC) is prepared with the composition as follows:

Active ingredient	25%(max)
Soprophor BSU	10%
Arylan CA	5%
N-methylpyrrolidone	50%
Solvesso 150	10%

The first three components are dissolved in N-methylpyrrolidone and to this is then added the Solvesso 150 to give the final volume.

EXAMPLE 2C

A wettable powder (WP) is prepared with the composition as follows:

Active ingredient	40%
Arylan S	2%
Darvan NO ₂	5%
Celite PF	53%

The ingredients are mixed and ground in a hammer-mill to a powder with a particle size of less than 50 microns.

EXAMPLE 2D

An aqueous-flowable formulation is prepared with the composition as follows:

Active ingredient	40.00%
Ethylan BCP	1.00%
Sopropon T360.	0.20%
Ethylene glycol	5.00%
Rhodigel 230.	0.15%
Water	53.65%

The ingredients are intimately mixed and are ground in a bead mill until a mean particle size of less than 3 microns is obtained.

EXAMPLE 2E

An emulsifiable suspension concentrate is prepared with the composition as follows:

Active ingredient	30.0%
Ethylan BCP	10.0%
Bentone 38	0.5%
Solvesso 150	59.5%

The ingredients are intimately mixed and ground in a beadmill until a mean particle size of less than 3 microns is obtained.

EXAMPLE 2F

A water dispersible granule is prepared with the composition as follows:

Active ingredient	30%
Darvan No 2	15%
Arylan S	8%
Celite PF	47%

The ingredients are mixed, micronized in a fluid-energy mill and then granulated in a rotating pelletizer by spraying with water (up to 10%). The resulting granules are dried in a fluid-bed drier to remove excess water.

EXAMPLE 2G

A dusting powder is prepared with the composition as follows:

Active ingredient	1 to 10%
Talc powder-superfine	99 to 90%

The ingredients are intimately mixed and further ground as necessary to achieve a fine powder. This powder may be applied to a locus of arthropod infestation, for example refuse dumps, stored products or household goods or animals infested by, or at risk of infestation by, arthropods to control the arthropods by oral ingestion. Suitable means for distributing the dusting powder to the locus of arthropod infestation include mechanical blowers, handshakers or livestock self treatment devices.

EXAMPLE 2H

An edible bait is prepared with the composition as follows:

Active ingredient	0.1 to 1.0%
Wheat flour	80%
Molasses	19.9 to 19%

The ingredients are intimately mixed and formed as required into a bait form. This edible bait may be distributed at a locus, for example domestic or industrial premises, e.g. kitchens, hospitals or stores, or outdoor areas, infested by arthropods, for example ants, locusts, cockroaches or flies, to control the arthropods by oral ingestion.

EXAMPLE 2I

A solution formulation is prepared with a composition as follows:

Active ingredient	15%
Dimethyl sulfoxide	85%

The active ingredient is dissolved in dimethyl sulfoxide with mixing and or heating as required. This solution may be applied percutaneously as a pour-on application to domestic animals infested by arthropods or, after sterilization by filtration through a polytetrafluoroethylene membrane (0.22 micrometer pore size), by parenteral injection, at a rate of application of from 1.2 to 12 ml of solution per 100 kg of animal body weight.

EXAMPLE 2J

A wettable powder is prepared with the composition as follows:

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Active ingredient	50%
Ethylan BCP	5%
Aerosil	5%
Celite PF	40%

The Ethylan BCP is absorbed onto the Aerosil which is then mixed with the other ingredients and ground in a hammer-mill to give a wettable powder, which may be diluted with water to a concentration of from 0.001% to 2% by weight of the active compound and applied to a locus of infestation by arthropods, for example, dipterous larvae or plant nematodes, by spraying, or to domestic animals infested by, or at risk of infection by arthropods, by spraying or dipping, or by oral administration in drinking water, to control the arthropods.

EXAMPLE 2K

A slow release bolus composition is formed from granules containing the following components in varying percentages (similar to those described for the previous compositions) depending upon need:

Active ingredient
Density agent
Slow-release agent
Binder

The intimately mixed ingredients are formed into granules which are compressed into a bolus with a specific gravity of 2 or more. This can be administered orally to ruminant domestic animals for retention within the reticulo-rumen to give a continual slow release of active compound over an extended period of time to control infestation of the ruminant domestic animals by arthropods.

EXAMPLE 2L

A slow release composition in the form of granules, pellets, brickettes or the like can be prepared with compositions as follows:

Active ingredient 0.5 to 25%
Polyvinyl chloride 75 to 99.5%
Diocetyl phthalate (plasticizer)

The components are blended and then formed into suitable shapes by melt-extrusion or molding. These composition are useful, for example, for addition to standing water or

for fabrication into collars or eartags for attachment to domestic animals to control pests by slow release.

EXAMPLE 2M

A water dispersible granule is prepared with the composition as follows:

Active ingredient	85%(max)
Polyvinylpyrrolidone	5%
Attapulgate clay	6%
Sodium lauryl sulfate	2%
Glycerine	2%

The ingredients are mixed as a 45% slurry with water and wet milled to a particle size of 4 microns, then spray-dried to remove water.

The following representative test method was used, applying the compounds of the invention hereinabove prepared.

The following representative test procedures, using compounds of the invention, were conducted to determine the pesticidal use and activity of compounds of the invention against certain insects, including aphids and nematodes. The specific species tested were as follows:

METHOD A: SYSTEMIC APHID SCREEN

Untreated cotton seeds were planted in a sandy loam soil and grown until the cotyledons were fully expanded. About 25 cotton aphids (*Aphis gossypii*) were transferred to each plant and 24 hours later the soil was drenched with test solution in aqueous acetone (99:1 v/v) at various soil concentrations and the plants maintained in a growth chamber. Six days after treatment the number of living aphids was assessed relative to an untreated control and a rating given (1 = 70-99% of untreated control, 3 = 31-69%, 4 = 1-30%, 5 = 0 aphids on the plant), and the LC50 values calculated. The following compounds gave a score of 3 or more at a concentration of 100ppm or less, or had an LC50 of 100ppm or less:

1, 2, 4-6, 8-10, 13, 15, 17-19, 21, 22, 24, 25, 28, 29, 31-33, 35-37, 41, 43, 50, 65, 67, 70, 80, 81, 84, 87, 88, 93-110, 113-119, 123, 126, 131, 133-135, 138, 139,

141, 144, 145, 147, 149, 150, 159, 161, 162, 164, 168, 171, 175, 182, 185, 186, 188, 240-243, 251, 252, 255 and 261-263.

METHOD B: NEMATODE TEST

Infected roots of tomato plants, containing egg masses of Southern root-knot nematode (*Meloidogyne incognita*), were removed from a stock culture and cleaned of soil, and the nematode eggs separated from the root tissue and rinsed with water. Samples of the egg suspension were placed on a fine screen over a receiving bowl, in which the water level was adjusted to be in contact with the screen. From the bowl, juveniles were collected on a fine screen.

Soil having 0-1% moisture content was placed in a cup. A stock solution of the test compounds in dimethylsulphoxide was prepared and diluted with water and the solutions thus obtained were applied to the soil at the rates of 250, 500 and 1000 g/ha. After 12-24 hours cucumber seeds were added and the soil and seeds mixed. An aqueous suspension of *Meloidogyne incognita* of approximately 300 second stage juveniles (J2) or approximately 2500 eggs was added to the soil. The cup was covered with a vented lid and maintained at 27°C and 80% relative humidity with a 14 hour photoperiod. Fourteen days later the roots were removed and evaluated for galling on a scale of 1, 3, 4 or 5 (1 = severe galling, equal to the untreated control; 3 = light galling; 4 = very light galling; 5 = no galling, complete control). Compounds scoring 3 or more were retested at multiple doses to give an ED3 value (effective dose to provide a 3 gall rating).

The following compounds gave a score of 3 or more at a concentration of 1000g/ha or less, or had an ED3 value of 1000g/ha or less:

1, 2, 13, 14, 20, 36, 38, 42, 46, 50, 52, 56, 58, 63, 69, 78, 83-85, 92, 98, 103, 121, 137, 140, 143, 152, 154, 156, 158, 167, 172, 178, 181, 185, 196, 206, 220, 222, 250, 254, 257 and 258.

METHOD C: Aedes Aegyptii TEST

Aqueous solution of *Aedes aegyptii* larvae were added to solutions containing known amounts of the test compounds in water containing < 10% of dimethylsulphoxide and kept at 20°C for 24 hours. The containers were tapped gently to stimulate the larval swimming response, and where little response to stimuli was observed the time since treatment was recorded. The ratings were 1 = inactive, 3 = moderately active, reduced

swimming with 30-70% mortality, and 5 = very active, little to no response to stimuli. The following compounds gave a score of 3 or more at a concentration of 100ppm or less:

2-16, 20-25, 27, 28, 30-34, 36, 37, 39-41, 43-45, 47, 48, 51-54, 56, 57, 59, 62, 66, 69, 71, 73, 75-77, 83, 85, 86, 89, 91, 110-112, 118, 120, 122, 127-129, 132, 136, 137, 140, 141, 146, 149, 153, 155, 157, 166, 170, 173, 174, 176, 177, 179, 180, 183-185, 188-194, 196, 200, 206, 216, 233-235, 237, 238, 245 and 249.

METHOD D: MUSCA DOMESTICA TEST

Aqueous sugar solutions (40%) were added to samples of known amounts of test compounds in dimethylsulphoxide solutions. Four *Musca domestica* pupae were then added to each sample and kept until the flies had emerged. Each test sample was rated as follows: 1 = 0-1 flies dead, 3 = 2-3 flies dead, 5 = 4 flies dead. The following compounds gave a score of 3 or more:

2-4, 6, 12, 13, 20, 34, 37, 51, 76, 83, 106, 110, 112, 118, 125, 140, 141, 146, 149, 153, 185, 189, 194-197, 199, 200, 204, 206-215, 233 and 258.

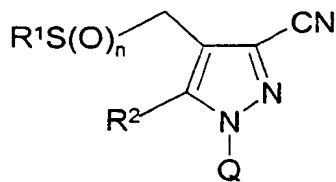
METHOD E: CAENORHABDITS ELEGANS TEST

Aqueous solutions of mixed life stages of *Caenorhabditis elegans* (free living nematode) were added to solutions containing known amounts of the test compounds in water containing < 1% of dimethylsulphoxide and kept at 20°C for 6 or 7 days. Visual assessment was then made, rating the population size and behaviour. The ratings were 1 = inactive, large population increase and behaviour similar to control; 3 = moderately active, population as many or slightly more and slow motion; 4 = active, population no to little increase and little movement; and 5 = very active, population no increase and no or little motion. The following compounds gave a score of 3 or more at a concentration of 100ppm or less:

5, 11, 15, 21-24, 28, 30, 33, 36, 39, 40, 43-45, 47, 48, 52-54, 56-66, 68-72, 74, 77, 79, 84-86, 89, 91, 97, 99, 103, 105, 106, 108, 112, 117, 120, 122, 125, 127-129, 142, 145, 146, 148, 151, 160, 163, 165, 168, 169, 176, 193-195, 198, 199, 201-203, 209, 217, 218, 236, 237, 245, 249, 259, 266 and 267.

Claims:

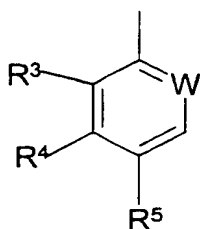
1. A compound of formula (I):



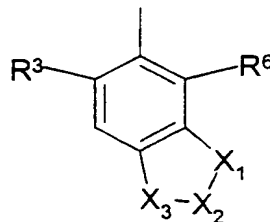
(I)

wherein:

Q is a group (A1) or (A2):



(A1)



(A2)

W is N or CR⁶;-X₁-X₂-X₃- is -CF₂CF₂O-, -CF₂OCF₂- or -OCF₂O-;

R¹ is alkyl, haloalkyl, alkenyl, haloalkenyl, alkynyl, haloalkynyl, cycloalkyl, cycloalkylalkyl or -(CH₂)_mR⁷; or is naphthyl optionally substituted by alkyl, haloalkyl, halogen, NO₂, alkoxy, haloalkoxy or R⁸S(O)_p;

R² is hydrogen, halogen or optionally substituted amino;R³ and R⁶ are each independently hydrogen or halogen;R⁴ is hydrogen or haloalkyl;R⁵ is hydrogen, halogen, haloalkyl, haloalkoxy, -S(O)_pCF₃ or SF₅;

R⁷ is phenyl or a five to seven membered heteroaromatic ring containing from one to four heteroatoms which may be the same or different selected from nitrogen, oxygen and sulphur, which ring is optionally substituted by R⁹;

R⁸ is alkyl or haloalkyl;

R^9 is alkyl, haloalkyl, halogen, CN, NO_2 , $R^{10}O$, $R^8S(O)_p$, $C(O)R^8$, $C(O)OR^{10}$ or $NR^{10}R^{11}$; or when R^7 is phenyl two adjacent R^9 groups together form a $-CF_2OCF_2-$ or $-OCF_2O-$ group;

R^{10} and R^{11} are each independently hydrogen, alkyl or haloalkyl; and m , n and p each independently have the values zero, one or two; or an agriculturally acceptable salt thereof.

2. A compound according to claim 1 in which R^2 is $-NR^{12}R^{13}$ or $-N=C(R^{10})(R^{14})$, wherein:

R^{12} and R^{13} are independently selected from hydrogen, alkyl, haloalkyl, alkenyl, haloalkenyl, alkynyl, haloalkynyl, $-C(O)R^{15}$ and $C(O)OR^{15}$; or R^{12} and R^{13} are joined together forming a divalent radical having 4 to 6 atoms in the chain, this divalent radical being alkylene, alkyleneoxyalkylene or alkyleneaminoalkylene;

R^{14} is alkoxy or haloalkoxy; or is phenyl optionally substituted by alkyl, haloalkyl, hydroxy, halogen, alkoxy, $-S(O)_pR^8$ or CN;

R^{15} is alkenyl, haloalkenyl, alkynyl or haloalkynyl; or is alkyl optionally substituted by halogen, alkoxy, $C(O)R^8$, $C(O)OR^{10}$, CN, $-S(O)_pR^8$, or $CONR^{10}R^{11}$.

3. A compound according to claim 1 or 2 in which R^1 is alkyl, haloalkyl, cycloalkyl or naphthyl; or phenyl optionally substituted by halogen, alkyl, haloalkyl, alkoxy, haloalkoxy or NO_2 ; or pyridyl optionally substituted by halogen or haloalkyl; or $-CH_2R^7$ where R^7 is phenyl optionally substituted by halogen, alkyl or alkoxy; or $-CH_2CH_2R^7$ where R^7 is phenyl.

4. A compound according to claim 1, 2 or 3 in which Q is a group (A1) wherein: W is N or CR^6 ; R^3 and R^6 are each independently hydrogen or halogen; R^4 is hydrogen; and R^5 is halogen, CF_3 , OCF_3 or SF_5 ; or wherein:

W is N or CR^6 ; R^3 and R^6 are each independently hydrogen or halogen; R^4 is CF_3 ; and R^5 is hydrogen.

5. A compound according to any one of the preceding claims in which R^2 is $-NR^{12}R^{13}$ or $-N=C(R^{10})(R^{14})$.
6. A compound according to any one of the preceding claims in which R^2 is $-NR^{12}R^{13}$ or $-N=C(R^{10})(R^{14})$, wherein R^{12} is hydrogen, alkyl or $-C(O)R^{15}$; R^{13} is hydrogen or alkyl; R^{10} is hydrogen; R^{14} is alkoxy; and R^{15} is alkyl.
7. A compound according to any one of the preceding claims in which n is 1 or 2.
8. A compound according to any one of the preceding claims in which:
 R^1 is alkyl, haloalkyl, cycloalkyl or naphthyl; or phenyl optionally substituted by halogen, alkyl, haloalkyl, alkoxy, haloalkoxy or NO_2 ; or pyridyl optionally substituted by halogen or haloalkyl; or $-CH_2R^7$ where R^7 is phenyl optionally substituted by halogen, alkyl or alkoxy; or $-CH_2CH_2R^7$ where R^7 is phenyl;
 Q is a group (A1) wherein:
 W is N or CR^6 ; R^3 and R^6 are each independently hydrogen or halogen; R^4 is hydrogen; and R^5 is halogen, CF_3 , OCF_3 or SF_5 ; or wherein:
 W is N or CR^6 ; R^3 and R^6 are each independently hydrogen or halogen; R^4 is CF_3 ; and R^5 is hydrogen; and
 R^2 is $-NR^{12}R^{13}$ or $-N=C(R^{10})(R^{14})$; wherein R^{12} is hydrogen, alkyl or $-C(O)R^{15}$; R^{13} is hydrogen or alkyl; R^{10} is hydrogen; R^{14} is alkoxy; and R^{15} is alkyl.
9. A compound according to any one of the preceding claims in which:
 R^1 is alkyl, haloalkyl, cycloalkyl or naphthyl; or phenyl optionally substituted by halogen, alkyl, haloalkyl, alkoxy, haloalkoxy or NO_2 ; or pyridyl optionally substituted by halogen or haloalkyl; or $-CH_2R^7$ where R^7 is phenyl optionally substituted by halogen, alkyl or alkoxy; or $-CH_2CH_2R^7$ where R^7 is phenyl;
 Q is a group (A1) wherein:
 W is N or CR^6 ; R^3 and R^6 are each independently hydrogen or halogen; R^4 is hydrogen; and R^5 is halogen, CF_3 , OCF_3 or SF_5 ; or wherein:

W is N or CR⁶; R³ and R⁶ are each independently hydrogen or halogen; R⁴ is CF₃; and R⁵ is hydrogen;

R² is -NR¹²R¹³ or -N=C(R¹⁰)(R¹⁴); wherein R¹² is hydrogen, alkyl or -C(O)R¹⁵; R¹³ is hydrogen or alkyl; R¹⁰ is hydrogen; R¹⁴ is alkoxy; and R¹⁵ is alkyl; and n is 1 or 2.

10. A pesticidal composition comprising an effective amount of a compound as defined in any one of claims 1 to 9, in association with an agriculturally acceptable diluent or carrier and/or surface active agent.

11. A method for the control of pests at a locus, which method comprises the application thereto of a pesticidally effective amount of a compound as defined in any one of claims 1 to 9 or a pesticidal composition as defined in claim 10.

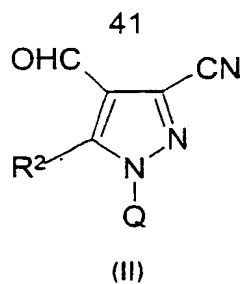
12. A method according to claim 11 wherein the locus is an area used, or to be used, for the growing of plants and the said compound is applied thereto at an application rate of from 2g to 5kg/ha.

13. Seed, treated or coated with an effective amount of a compound as claimed in any one of claims 1 to 9 or a pesticidal composition as claimed in claim 10.

14. Use of a compound as claimed in any of the claims 1 to 9 or a composition as claimed in claim 10 for controlling pests.

15. Use of the compound as claimed in any of claims 1 to 9 for preparing a veterinary medicine.

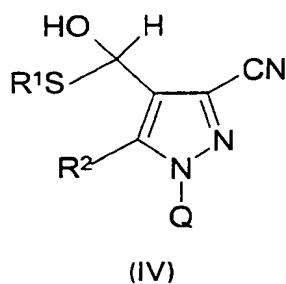
16. A process for the preparation of a compound of the formula (I) as claimed in any of claims 1 to 9, which comprises reacting a compound of the formula (II),



wherein R^2 and Q are defined as in claims 1 to 9, with a thiol of formula (III):



wherein R^1 is as defined as in claims 1 to 9, in the presence of a Lewis acid, to give a hemithioacetal intermediate of formula (IV):



which is optionally isolated, and is treated with a reducing agent and, optionally, oxidising the resulting compound.

INTERNATIONAL SEARCH REPORT

International Application No

PCT/EP 01/02306

A. CLASSIFICATION OF SUBJECT MATTER

IPC 7 C07D231/38 C07D401/12 A01N43/56

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 7 C07D A01N

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

EPO-Internal, PAJ, CHEM ABS Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

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A	PATENT ABSTRACTS OF JAPAN vol. 1997, no. 03, 31 March 1997 (1997-03-31) -& JP 08 311036 A (TAKEDA CHEM IND LTD), 26 November 1996 (1996-11-26) compounds 106-114, page 50/51 abstract -----	1-15



Further documents are listed in the continuation of box C.



Patent family members are listed in annex.

* Special categories of cited documents:

- *A* document defining the general state of the art which is not considered to be of particular relevance
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- *T* later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
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Date of the actual completion of the international search

2 August 2001

Date of mailing of the international search report

13/08/2001

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INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/EP 01/02306

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